Corrosion of Steel in the Arabian Environment

by

Uthman M. Dawoud

A Thesis Presented to the

FACULTY OF THE COLLEGE OF GRADUATE STUDIES

KING FAHD UNIVERSITY OF PETROLEUM & MINERALS

DHAHRAN, SAUDI ARABIA

In Partial Fulfillment of the
Requirements for the Degree of

MASTER OF SCIENCE

In

CHEMICAL ENGIEERING

July, 1975

Order Number 1355734

Corrosion of steel in the Arabian environment

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King Fahd University of Petroleum and Minerals (Saudi Arabia), 1975

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M. S. Thesis

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July 8 , 1975

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M. S. THESIS

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGEE OF MASTER OF SCIENCE IN CHEMICAL ENGINEERING.

TITLE : CORROSION OF STEEL IN THE ARABIAN ENVIRONMENT

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ACKNOWLEDGEMENT

The research described in this thesis was carried out in the Department of Chemical Engineering at the University of Petroleum & Minerals under the supervision of Professor E.G. Peattie. I am extremely grateful to him for his advice, guidance and many helpful discussions.

I am indebted to many others, including faculty and technicians, and I wish to record here my sincere thanks for their invaluable assistance.

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LIST OF FIGURES

LIST OF SYMBOLS USED

A	:	Area, Square Decimeter
C	:	Constant for T.D.S. (explained later)
D	:	Diameter, Decimeter
d	:	Difference between two numbers
L	:	Length
md	:	Decimeter
mdd	:	Milligrams per sq. decimeter per day
ml	:	Millileter, unit of volume
mpy	:	Mils per year (1 mil = 0.001 inch), Unit of corrosion rate
N	:	Total number of test run
pAIK	:	pH of alkaline solution
pCa	:	pH of Ca^{++} solution
ppM	:	Parts per million, unit of concentration
R	:	Rate of Corrosion, mils per year (1 mil = 0.001 inch)
r	:	Coefficient of Correlation (1) Rank (Spear man) (2) Product-Moment Coefficient (Pearson)
T.D.S.	:	Total dissolved solids
t	:	Time, days
w	:	Width, decimeter
W	:	Weight loss, grams
( )	:	Reference numbers in parentheses.

ABSTRACT

Samples of water were taken from various locations in the Eastern Province of Saudi Arabia and were analyzed for chemical composition particularly dissolved Oxygen. These waters were subjected to an accelerated corrosion test to classify their corrosivity, and the measured corrosion rates subjected to correlation checks against the chemical species in the sample. It was found that bicarbonate and a negative Longelier Index of the waters were the chief contributors to the corrosion. Treatment with lime or removal of oxygen are methods recommended to control the corrosion rate.

INTRODUCTION

Production of oil and other industries in Saudi Arabia has required the use of drilling pipes, flow lines, and equipment made of steel. This metal corrodes in the man-made as well as natural environment such as, sea water, soil, sour crude oil, atmosphere, ground water.

Up to 1973, ground water was considered to require no corrosion protection since studies in 1954 on the North Bugga Injection Wells had shown no pronounced corrosion rates nor abnormal content of dissolved oxygen in the water.

Recently, because of the extention of oil production facilities, it has been found that the water in Berri field, Souther Ghawar field, and in other areas in the Eastern Province cause serious corrosion problems. The discussion of this thesis will be restricted to a study of the corrosivity of the ground waters in various areas of the Eastern Province.

CHAPTER 1

SURVEY OF LITERATURE

The basic work on water corrosion was carried out by Baylis (1) in the United States. The purpose of his research was to develop techniques to reduce corrosion in public water supplies. He found that the water in many of the public supplies caused fairly rapid deterioration of the iron pipes unless it had been treated with an alkali. His most important finding was that saturation by $CaCO_3$ (typically 100 p.p.m.) greatly reduced corrosion rates. Two parallel mechanisms were proposed to explain this. One, simple chemical inhibition of the corrosion process, and two, the build up of a film, preventing physical contact between the iron surface and the water. He recommended that line should be used for treating the water if the concentration of $CaCO_3$ is less than about 30 p.p.m., but if the concentration of $CaCO_3$ is above 30 p.p.m. then either lime or might be used.

Similar studies was carried out by Tilman (2) in Germany.

A contemporary study of water was carried out by W.F. Langelier (3). His paper discussed certain chemical relationships involved in the action of natural oxygen containing waters on the interior of iron and galvanized pipe (propose analytical control of preventive treatment).

He classified ground waters into two major groups and developed the well known Langelier Index, sometimes called the Saturation Index. His studies showed that a positive Index indicates over-saturation and a tendency to crystallize or to laydown a protective coating of $CaCO_3$ in the pipe. A negative Index indicates under-saturation or a tendency to dissolve the existing carbonate coating. A rise in temperature increases the numerical value of the Index, which will increase the corrosive activity of the water.

The effect of dissolved oxygen and carbondioxide on corrosion of steel, was studied by Skaper and Uhlig (4). They showed that both dissolved carbon dioxide and oxygen increases the rate of corrosion, and corrosion by a solution containing both CO_2 and O_2 is ten to forty percent higher than the sum of the corrosion by the dissolved gases acting individually.

The affect of the pH value was studied by Whitman, Russell, and Altieri (5). They found out that there is a fairly wide range over which variations in hydrogen-ion concentration (at $CaCO_3$ saturation) of a solution have no effect on the rate of corrosion. This range extends from a pH of about 10 to 4.1 at 22°C and from 9 to 4.3 at 40°C. Variation of pH however will have a secondary effect, in that the $CaCO_3$ saturation is a function of pH and that corrosion rates are strongly dependent on the concentration of $CaCO_3$.

CHAPTER 2

PURPOSE OF RESEARCH

The main objective of this study has been to classify the waters in the Eastern Province according to their corrosivity using standard methods for measuring corrosion. Samples were taken from different locations in the region and a complete chemical analysis made.The waters were subjected to an Accelerated Corrosion Test to determine relative corrosion rates, and results correlated against the composition of the waters to determine which components, if any, are causing or inhibiting corrosion. It was hoped that the results might suggest methods of controlling corrosion rates.

CHAPTER 3

EXPERIMENTAL

3.1 Field Work

Samples of ground waters were collected in 5 liter plastic containers from the following sites :

Sample No. 1 - from the Ice Company Well in Al-Jubail.

Sample No. 2 - from Qashuria Well in Qatif

Sample No. 3 - from A'm-Ammar Well in Qatif.

Sample No. 4 - from the University of Petroleum & Minerals in Dhahran.

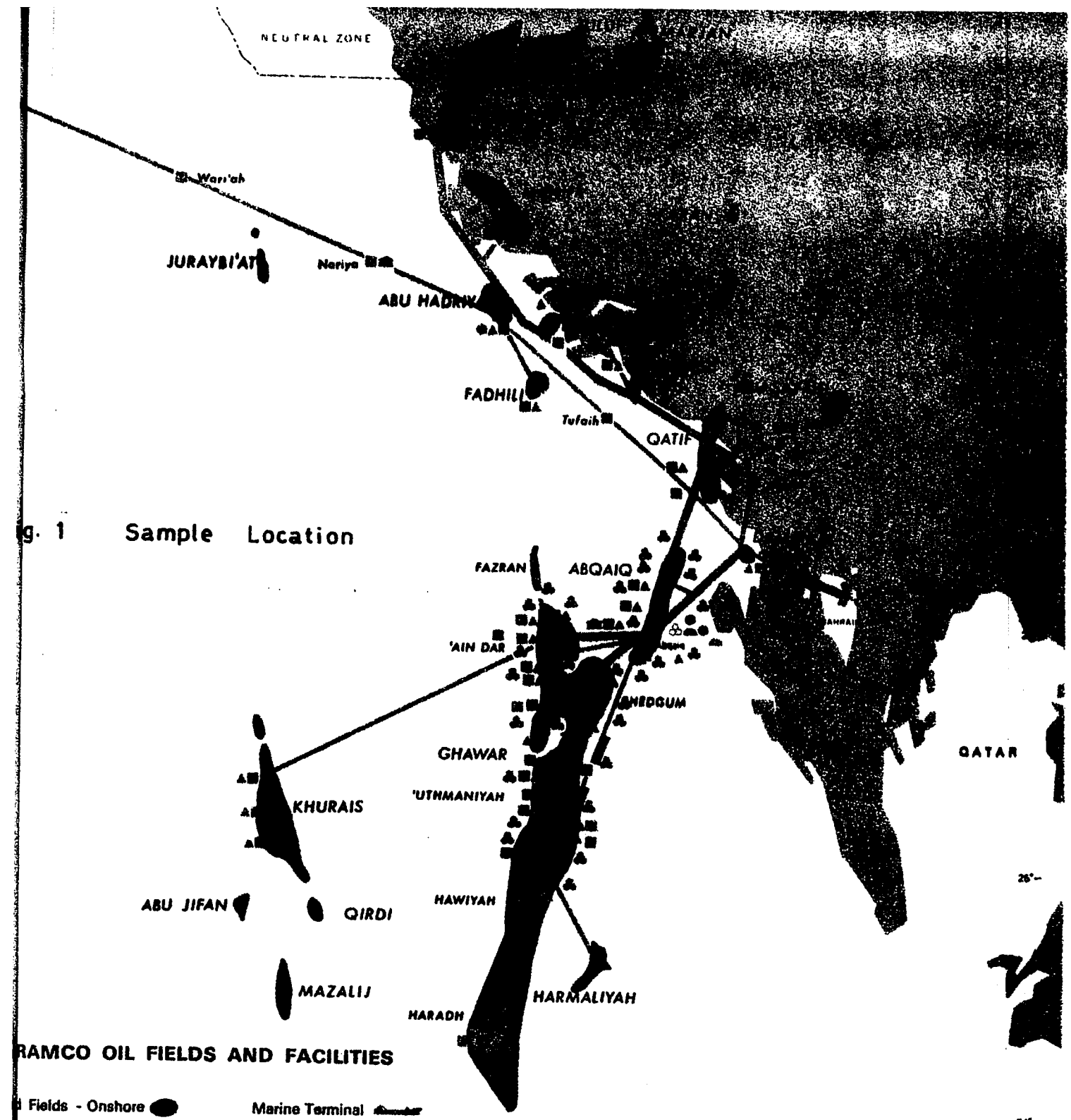
Sample No. 5 - from the cement company well in Hofuf.

Sample No. 6 - from the Saudi Arabian Fertilizer Company (SAFCO) in Dammam.

The sites are shown in fig. (1)

3.2 Laboratory Work

The amount of oxygen as well as certain anionic and cationic species dissolved in ground-water play a very important role in the corrosivity. Therefore rigorous analysis of the water samples was necessary and these are presented in tables (1) and (2). The analytical procedure is discussed in the following sections.

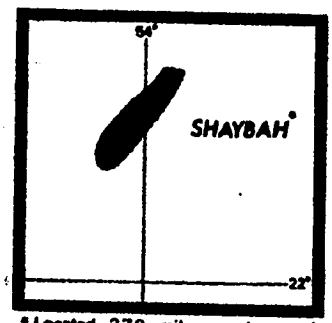


g. 1 Sample Location

RAMCO OIL FIELDS AND FACILITIES

- Fields - Onshore
- Fields - Offshore
- Proved Fields Onshore/offshore
- Refinery
- Stabilizer
- Gas-Oil Separator
- Pump Station
- Marine Terminal
- Sea Island
- Pipeline
- Multiple Pipeline System
- Gas Injection
- Water Injection
- LPG Plant
- Storage

KILOMETERS



*Located 370 miles southeast of Dhahran in the Sand Mountains of the Rub' al-Khali.

3.2.1 Dissolved Oxygen Content

Refer to fig. (2)

3.2.1.1 Description of Apparatus

The apparatus consists of two parts, the Oxygen Analyzer and the Sensor. The system operates on the polarographic principle. This is briefly described below :

1. When the sensor is placed in the sample, oxygen from the sample diffuses through the telfon membrane, which separates the sample from the internal polorographic cell.

2. Diffused oxygen is reduced electrochemically (consumed) in the cell, causing current flow proportional to the partial pressure of oxygen in sample.

3. The sensor sends a signal to the Oxygen Analyzer which is amplified and processed for read out.

3.2.1.2 Procedure for Calibration

Refer to table (1) and fig. (3).

1. The sensor was exposed to a well agitated water sample and the reading taken. Care was taken to maintain the sensor full with sample water all the time.

2. Another sample of the same water was analyzed by Winkler method (6) for dissolved oxygen content.

3. The dissolved oxygen content using the Winkler method was calculated in parts per million, see Appendix B.

4. With the range switch at 25% the calibrat control was adjusted to the reading of step 3. The scale used was 0-10, since dissolved oxygen is not expected to exceed 10 ml/liter of water.

5. A maximum reading equivalent to oxygen saturated water, was established. This was accomplished as follows :

   One liter of distilled water was cooled to 0°C, and Oxygen gas bubbled into the cooled water until a constant reading was achieved. This was called sample # 7. The sample was analyzed by the Winkler method and the Oxygen Analyzer at room temperature (25°C).

6. For minimum reading on the analyzer, equivalent to zero dissolved oxygen, another sample was prepared (sample No. 8) by boiling two liters of distilled water to strip the dissolved oxygen from the water.

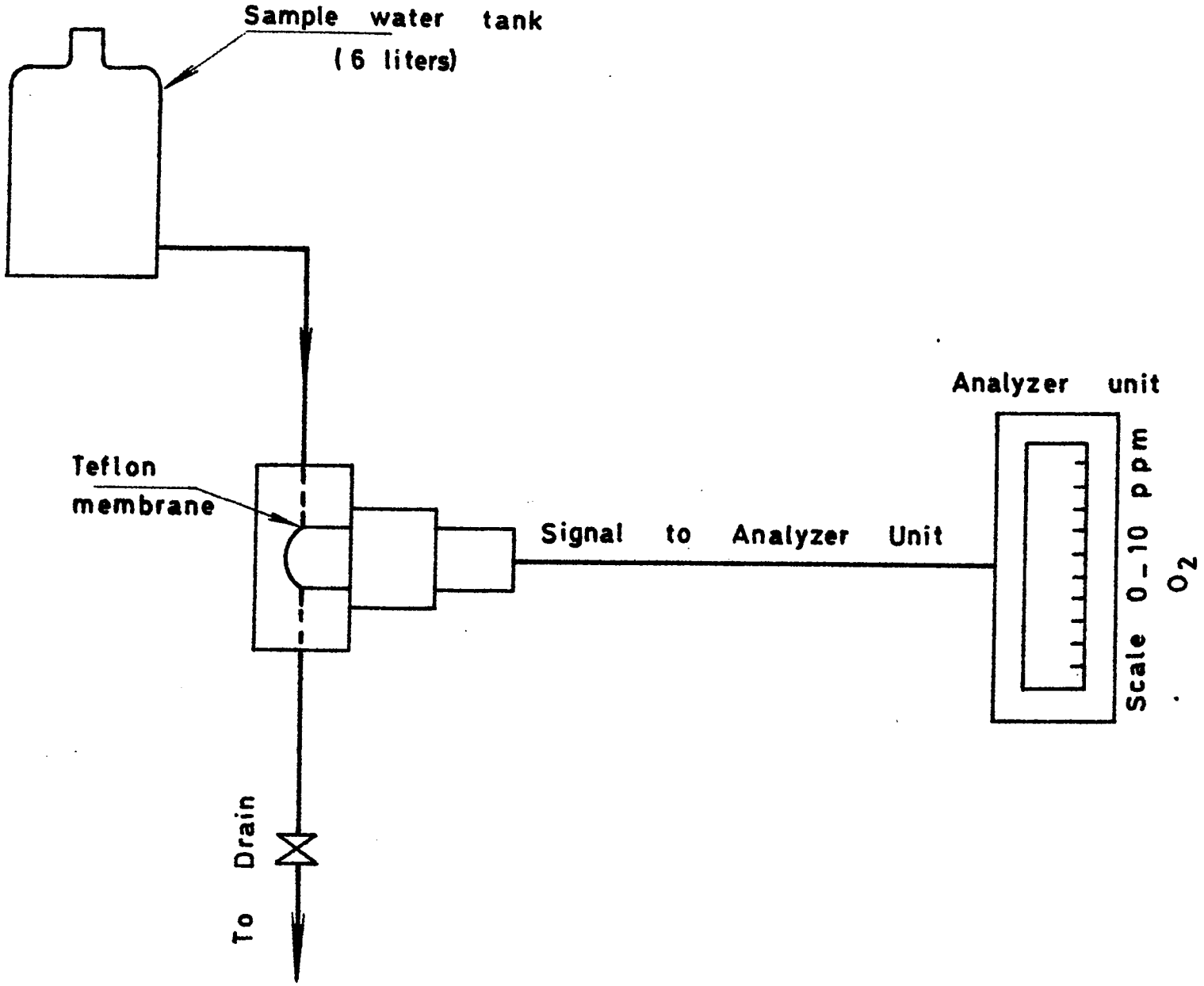


Fig. 2 Sketch of Dissolved Oxygen Apparatus

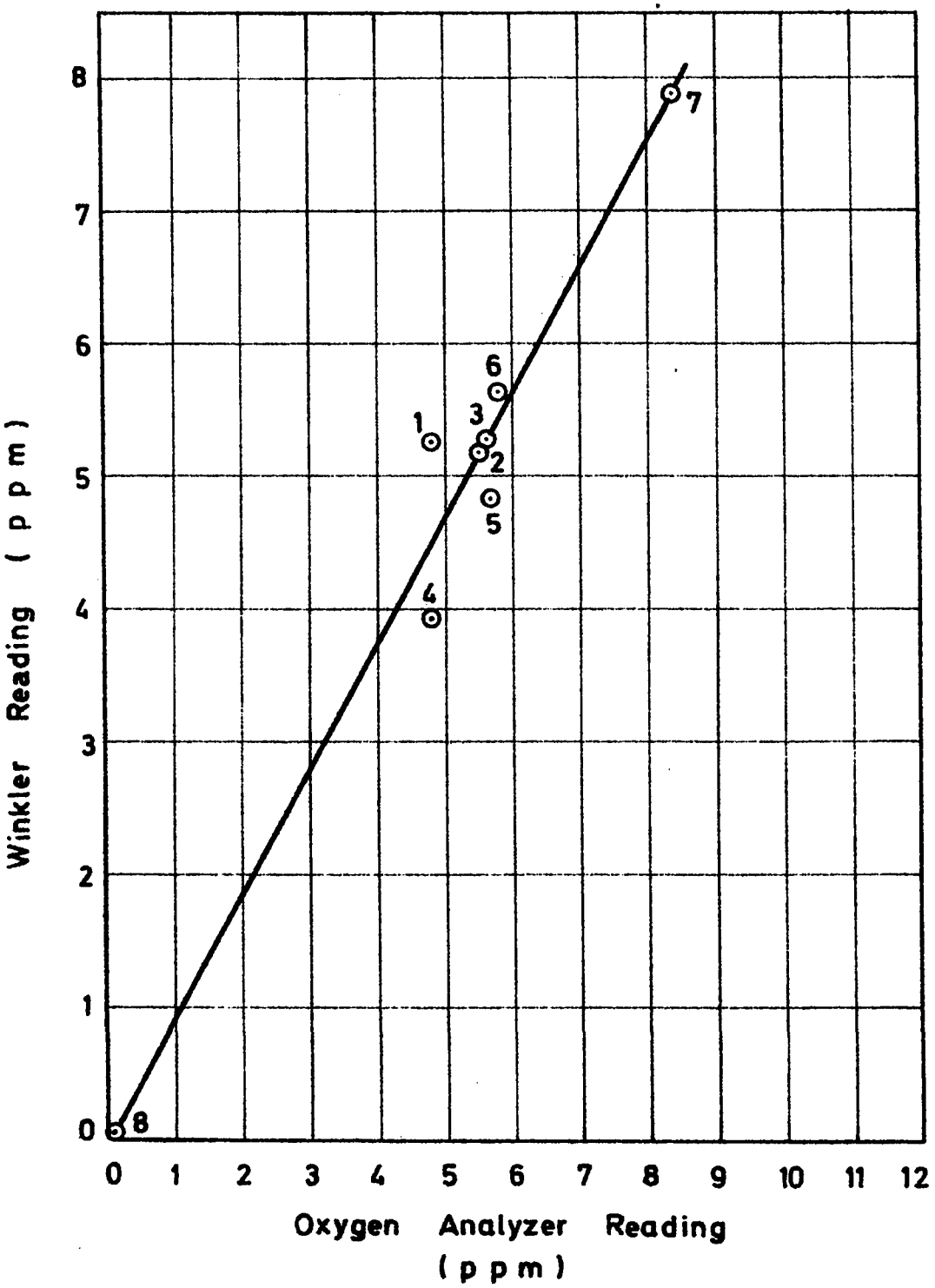


Fig. 3 Calibration chart for the oxygen analyzer .

To this sample 10 ml of Hydrozine were added to absorb any dissolved oxygen remaining.

7. From these three points the calibration curve was constructed, fig. (3)

3.2.1.3 Determination of Dissolved Oxygen

The dissolved oxygen of the other samples were found by using the reading of the oxygen analyzer and the calibration chart. Care was taken to maintain the sensore full with sample water all the time.

3.2.2 Chemical Analysis

The six sample of waters that were collected from different areas mentioned in section 3.1 were analyzed chemically to determine which anions and cations were present. Table (2) is a summary of the analysis. The method for determination of CO_3, HCO_3, and SO_4 was similar to that used by Vogel (7). For Na^+, Ca^{++}, Mg^{++}, and k^+ the Varian Techtron model AA-5 Atomic Absorption Apparatus was used. All the analyses were made during the period March 1-8, 1975.

3.2.3 Accelerated Corrosion Test

To calculate the relative rates of corrosion in the waters, it was decided to use a simple electrolytic cell consisting of a steel anode and a copper cathode with a particular water as the electrolyte. Corrosion rates could then be determined by running a time exposure test on the cells of all the waters. The corrosion rates were measured against a control cell with distilled water as electrolyte. The original weights of the electrodes were determined using a Mettler balance Type H-8 with accuracy of (±0.002). The cells were then connected on March 25, 1975 and allowed to operate until May 11, 1975, a period of 44.9 days. Precautions were taken to ensure the temperatures would remain constant during this period. Potential difference readings were taken at the beginning of the test, at the mid-point (April 15,1975) and at the end of the test before disassembly.

3.2.3.1 Material Description

A Venier-Caliper was used for all measurements with accuracy of (±0.002). Refer to fig. (4).

1. Eight square, carbon steel coupons of standard size, 2 inches x 2 inches, were selected. They were numbered from 1 to 8 at the upper left corner.

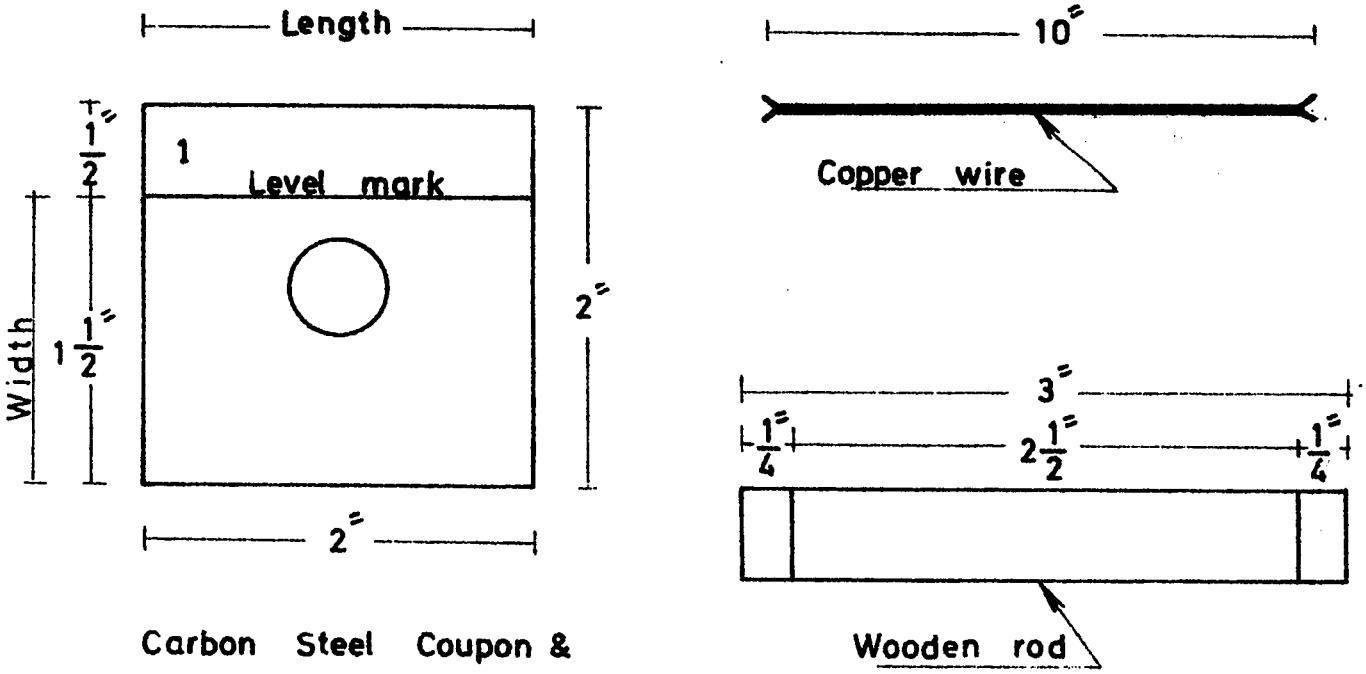
2. Eight, square, copper coupons of standard size 2 inches x 2 inches, were selected as cathode. They were also numbered from 1-8 at the upper left corner.

3. A hole 1/2" in diameter was made in the middle of each coupon. The purpose of this hole was to support and separate the steel and copper coupons by a wooden rod.

4. Eight wooden rods 3 inches long and 1/2 inch in diameter were made each with a mark of 1/4 inch from each end. The purpose of this mark was to indicate the standard distance between the coupons.

5. Eight copper wires 10 inches long and 0.025 inches in diameter were used to connect the coupons in the cells. Crocodile clips were soldered to the two ends of the all the wires to facilitate breaking the circuit during the test for any electrical measurements.

6. All the steel and copper coupons were marked by a line under their numbers. The purpose of this line was to standardise the water level in the cells. Had the whole coupon been covered by the



Carbon Steel Coupon &
Copper Coupon

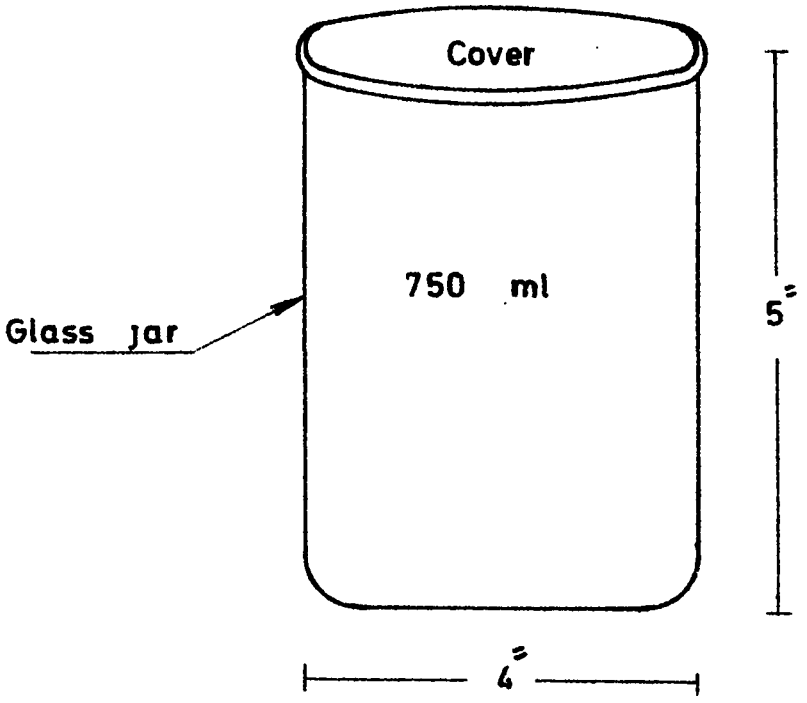


Fig. 4 Sketch & Size of material used for making the test.

water sample, the clips and the copper wire would have corroded and this would have affected the corrosion rate of the steel coupons themselves.

7. Eight glass jars, 750 ml in volume and 5 inches x 4 inches were used as the container of the cells.

3.2.3.2 Original Data

Refer to tables (3), (4) and (5), Appendix A.
To calculate the rate of corrosion, it was necessary to know the original weight of coupons, the exact dimensions of the coupons, the time when the circuit of each cell was closed, and other auxiliary data. The procedure for collection of this data is outlined below:

3.2.3.2.1 Original Weight

1. The steel coupons and copper coupons were soaked in kerosene to dissolve any undesired material from the surface.

2. The coupons were cleaned by an eraser while they were wet.

3. The coupons were further cleaned by rubbing very gently with emery cloth.

4. The coupons were dried in a desiccator for 3 hours.

5. The coupons were weighed with an electrical balance, Metler, model H8. Original weights are recorded in table (3), Appendix A.

3.2.3.2.2 Coupon Dimensions

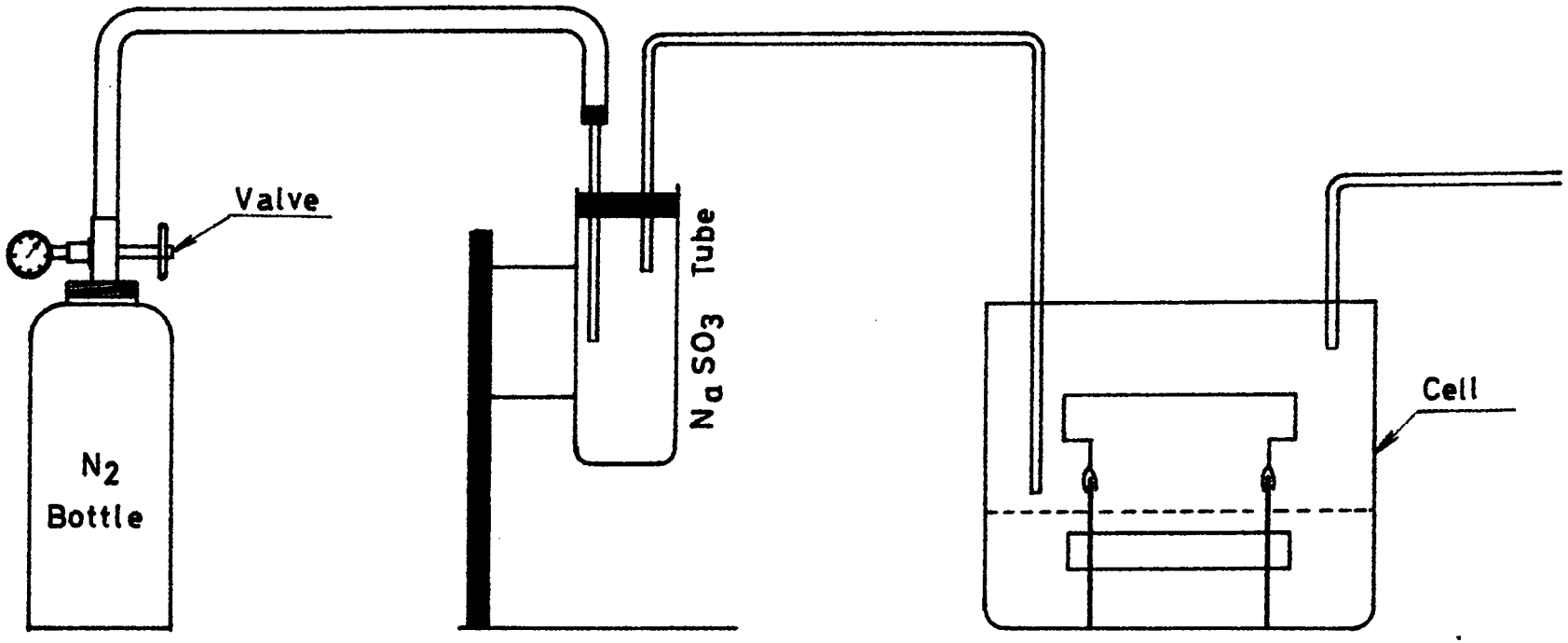
Refer to table (3), and fig. (6)
The length of the coupons, were measured at the water level mark. The width was considered to be the distance from the base of the coupon up to the level mark. A vernier caliper was used to measure the length and width of coupons and also to measure the diameter of the hole of the coupons.

3.2.3.2.3 Elapsed Time

The time of closing the circuit in the cells was recorded as the time of starting the corrosion test (see section 4.2.4, stop 6).

3.2.3.3 Cell Construction

Refer to fig. (5) & (6) and table (4).



Purging Apparatus

Fig. 5 It shows the apparatus used for purging the cells with N_2 gas.

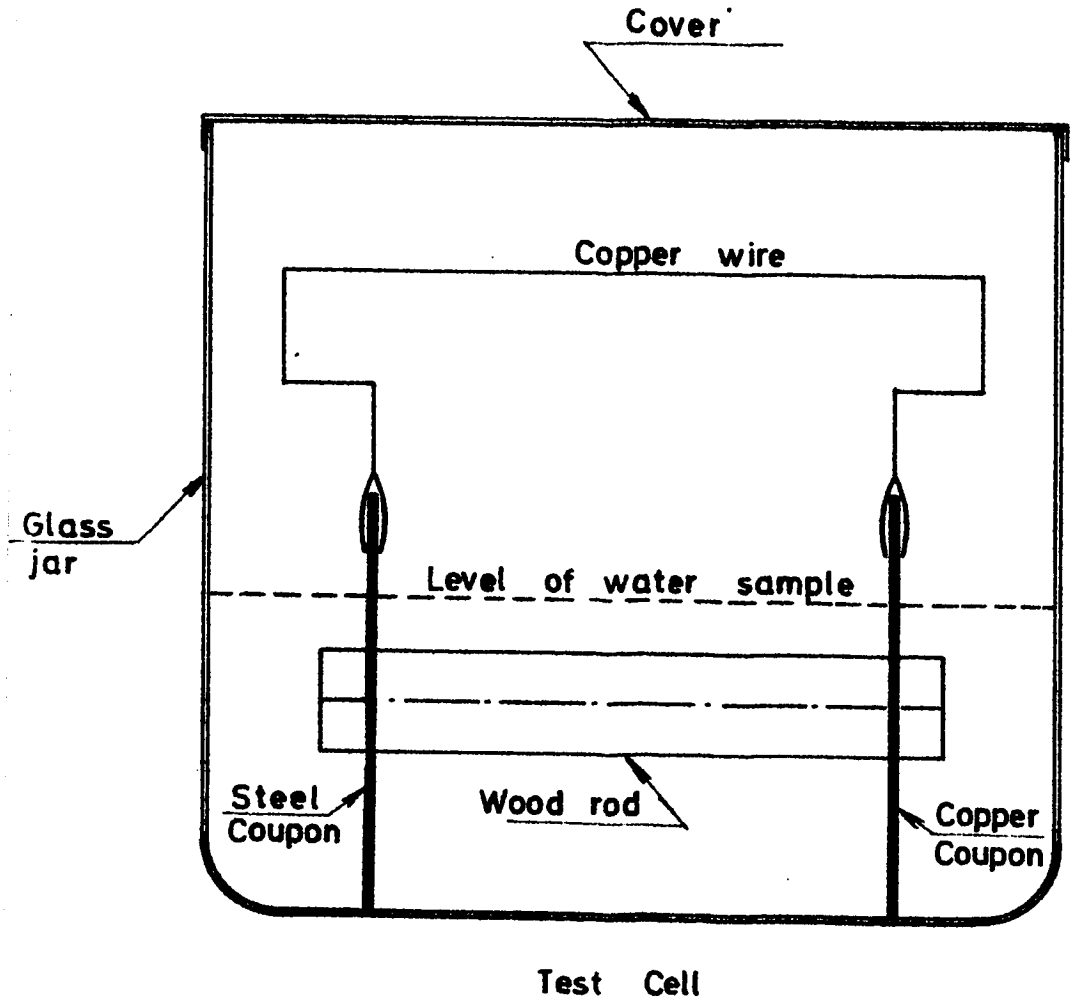


Fig. 6 Sketch of the cells used for making the test.

Eight corrosion test cells were set up to study the corrosivity of the eight water samples mentioned in section 3.1 and 3.2.1.2. Cell No.1 is taken as an example of the procedure used in constructing the other cells. This was as follows:

1. Steel coupon # 1 and copper coupon # 1 were inserted in wooden rod # 1 up to the mark of insertion.

2. The two coupons were put in the glass jar # 1. The cell was purged with N_2 to strip any air in it.

3. Sufficient sample water, 280 ml, to cover the coupon, up to the level mark was poured into the jar.

4. The potential difference of the open circuit was measured by potentiometer ± 0.01 m.v. (Leeds & Northrup).

5. The two coupons were connected by the copper wire # 1. That is to say, the circuit was closed.

6. The time of closing the circuit was recorded. All the cells were connected at the same time on March 29, 1975 at 1:30 p.m. and kept for 45 days.

7. The potential difference between the electrodes was measured at the middle of the test (April 15, 1975) and at the end of the test (May 11, 1975).

3.2.3.4 Final Data

Refer to tables (4), (5) and (6).

To find the rate of corrosion of steel coupons based on weight loss it was necessary to know the time of opening the circuit in each cell, and the final weight of the corroded steel coupons. The procedure adopted is explained below :

1. The eight circuits were opened on May 11, 1975 at 9:00 p.m.

2. The coupons were removed from the cells and kept in a dessicator for three hours for drying.

3. The coupons were cleaned in the manner described in steps 2 and 3 of section 3.2.3.2.1.

4. The coupons were weighed.

5. The pH of the filtered water samples was measured.

6. The loss of weight was calculated and the corrosion rate was determined using the methods described in Appendix B-4.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Results

Experimental results are presented in Tables (2), (3), (4), (5), (6) and (7). Appendix A.

A series of correlation coefficients have been calculated using the procedure of Spearman (9). These indices were used to determine what significant characteristics of the ground waters had the most effect on the corrosion rate. The methods used in the calculation are shown in Appendix B-6 while the interpretation of the results is in Chapter 6.

4.2 Discussion of Results

Based on examination of the chemical composition of the waters and the relative corrosion rates, it can be seen that certain components apparently have a significant effect on the corrosion rate and others seem to have very little. Discussed in order they are :

1. pH value
2. Dissolved Oxygen
3. Conductivity
4. Calcium and Magnesium

5. Bicarbonate Effect
6. Langelier Saturation Index
7. Other Ions

4.2.1 pH Value

Table (6) shows the pH values of the waters at the beginning and the end of the 44.9 day test compared with the corrosion rates. Certain characteristics are noticeable :

1. The highest corrosion rate (8.1) coincided with the lowest pH (6.8)

2. The average change in pH of the natural waters during the period of test was 2.03 (from 7.06 to 5.03). This shift to acidity indicates a side effect of the corrosion process.

3. The distilled waters did not change in pH during the test whether oxygen saturated (pH = 7.0) or oxygen free (ph.7.3)

4. A correlation coefficient calculated for the values of pH vs. the corrosion rate was (-0.69), indicating a trend but not a method for predicting the corrosion extent.

4.2.2 Dissolved Oxygen

Table (2) shows certain relationships between dissolved oxygen and corrosion rate. They are not entirely what would be expected from the literature. For example, Uhlig (10) obtained a linear relationship between the concentration of dissolved oxygen and the rate of corrosion of iron.

The results of the tests presented here show no such relationship. It is believed that the other dissolved species completely mask the effect of the oxygen.

Sample eight (oxygen free distilled water) showed the lowest corrosion rate (9 mdd). This is consistent with the literature. For example Uhlig (10) found that at very low concentration (0.8 ml/liter O_2) the corrosion rate was about 10 mdd.

The dissolved oxygen of the ground waters averaged 5.6 ppm with a range from 4.8 to 5.8. The results indicate that this does not have any measurable effect on the corrosion rate.

The correlation coefficient calculated between the percentage of dissolved oxygen and the corrosion rate of the eight

samples showed (-0.12), very close to random value. If the distilled water samples (sample 7 & 8) are omitted from the correlation and only the six ground waters (samples 1 to 6) compared with the corrosion rate, the results are even more negative, (-0.21). This strongly suggests that the presence of oxygen is required for a corrosive condition to exist, but that it is not the major rate determining parameter.

4.2.3 Conductivity

The conductivity of the waters was an average of 47 microohms but with one value as high as 74. This value did not correlate with either the highest or the lowest corrosion rate. The conductivity of the distilled water compared with the corrosion rate showed a correlation coefficient of 0.66, a positive indication but not a complete one, since the oxygen saturated distilled water showed the least conductivity (10 microohms) but not the lowest corrosion rate.

4.2.4 Calcium and Magnesium

Because of the importance of calcium as a corrosion inhibitor, it was thought that there might be a

relationship between the corrosion rate and the lack of calcium. No such relationship was found. Moreover, the total amount of Ca^{++} and Mg^{++} (also present in relatively large quantities) also revealed no significant correlation.

The correlation coefficient for Calcium was 0.76 while that for Magnesium was 0.75. These indicate a positive (retarding) rather than a negative effect on corrosion rate.

4.2.5 Bicarbonates

No carbonates were found in the Arabian ground waters but the bicarbonate (HCO_3^-) content ranges from 134 to 237 ppm. This shows the largest correlation coefficient (0.88) of any of the chemical components of the waters tested. The bicarbonate content at low concentrations had a significant effect on the corrosion rate even more than that of oxygen. However, at high concentrations close to saturation, its action is reversed,

4.2.6 The Langelier Saturation Index

As has already been discussed in the literature search, the basic work of Tillman (2) on bicarbonate attack on steel and Baylis (1) on calcium carbonate equilibrium curves led

Langelier (3) in 1936 to develop the Saturation Index, which is defined as : see fig. (7), page 51.

$$\text{Index} = pH_{(\text{measured})} - pH_s$$

where pH_s= pH at an equilibrium of Ca^{++} alkalinity and $CO_3^{=}$ activity.

This property may be calculated as shown in Appendix B-5.

Using data from the water analyses, the saturation indices were calculated for the waters tested and are shown in Table (6) compared to the corrosion rates. These are negative for all the tested Arabian waters and zero (in equilibrium) for the two distilled waters used. According to Uhlig (11) a negative index shows a tendency toward corrosion.

The correlation coefficient between the bicarbonate Saturation Index and the corrosion rate is 0.92. This indicates the following :

a. Low bicarbonate concentrations are consistent with high corrosion rates. This supports the conclusion drawn in part (5).

b. The corrosion rate is more pronounced as the negativity of the Index increases.

4.2.7 Other Ion Effects

The other Ions in the waters show the following correlation coefficients :

Species	r
K^+	0.66
Na	0.69
Cl^-	0.71
$SO_4^=$	0.61

(There is no $CO_3^=$)

All these are positive, indicating some effect on the corrosion but none is large enough to affect the corrosion significantly. The total dissolved solids has more effect, having a correlation coefficient of 0.80 suggesting certain interactions.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

1. There is very little variation in the chemical composition or corrosion tendencies of the ground waters sampled at various locations in the Eastern Province of Saudi Arabia.

2. The differences in corrosion may be predicted from the varying Langelier Indices. These require analyses of calcium, bicarbonate and total solids for computation.

3. The range of corrosion rates vary from 8.10 to 6.54 mils per year at different locations, but all are greater than the corrosion rate in oxygen saturated distilled water (4.7 mils per year).

4. The principal cause of corrosion is carbonic acid (bicarbonate). In these waters the concentration of the bicarbonate is not high enough to form a self inhibiting protective film. Oxygen is a contributory factor.

5.2 Recommendations

The recommendations are divided into two parts :

1. Recommendations for reducing the corrosion caused by Arabian ground waters.

2. Recommendations for further work on this general problem.

5.2.1 Recommendations for reducing Corrosion

As has been shown above, the evidence points to under saturated soft ground water as the cause of the corrosion. This condition is indicated by the negative Langelier Saturation Index. It may be adjusted by any one of the following methods :

5.2.1.1 Treatment with Lime ($Ca(OH)_2$)

According to Uhlig (12) addition of slaked lime ($Ca(OH)_2$) will have two effects: first it will react with the acidic bicarbonate to neutralize the acidity and second, it will form a protective coating of calcium carbonate ($CaCO_3$) on the surface of the metal exposed to the water. The economics of this time treatment will have to be studied further. However, since it is standard procedure

for many municipal water treatment plants, it should not be hard to develop a continuous injection system. This is the method originally developed by Baylis in 1913 referred to by Speller (13).

5.2.1.2 Removal of Oxygen from the Water

Sample 8 (oxygen free) had the lowest corrosion rate, which suggests that removal of oxygen from the water will cut down the corrosion. In a closed system this may be achieved simply by de-aerating the water. Various methods have been developed to do this, for example, scrap iron deaeration, heating and mechanical deaerators. These have been discussed by Speller, (14), (15) and (16).

5.2.1.3 Cathodic Protection

The exterior of well casing exposed to corrosive waters may be protected from corrosion by impressing a direct current on the steel. The interiors cannot be protected unless a complicated anode system is used and this is usually more expensive than the cost of the casing Uhlig (17).

5.2.1.4 Inhibitors

Certain chemical inhibitors usually chromates or phosphates may be injected into the system. These form a thin film on the surface of the metal. Their use is justifiable only in a closed system Uhlig (18). Also, they are sometimes poisonous and cannot be used for drinking water.

The consensus is that the lime treatment should be the most economical.

5.2.2 Recommendations for Further Work

The above problem represents only a small phase of the general problem in the use of ground water in Arabia. Additional work will be necessary before the problem is completely resolved. This work should include :

5.2.2.1 Wider Selection of Water Samples

Most well water from the Eastern Province is from the Wasia zone. It would be informative to examine water from other sources, for example Abqaiq, Fazran, Uthmaniyah and Khurais.

5.2.2.2 Use of Coupons at the Site

In order to augment the accelerated corrosion tests used, it would be advisable to suspend test coupons, similar to those used for ordinary non-accelerated exposure tests in the waters under field conditions. These should duplicate our laboratory tests at least in rank. Normally at least six months exposure would be necessary to get meaningful results.

5.2.2.3 Use of Corrosometer probes

In addition to coupon data, it is the custom in industry to install corrosion meter probles in areas suspected of corrosivity. These probes may be checked periodically to measure the extent of corrosion. It is recommended that such an instrument should be used in further studies.

5.2.2.4 A study of the corrosion rate in distilled water containing various concentrations of dissolved oxygen.

5.2.2.5 A study of lime treated natural waters to quantify the effects on corrosion rate.

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APPENDIX

APPENDIX A

Tables of Results

TABLE (1)

CALIBRATION OF OXYGEN ANALYZER
WINKLER METHOD VS THE OXYGEN
ANALYZER READING

Sample No.	Winkler Method Reading (ppm)	Oxygen Analyzer Reading (ppm)
1	5.27	4.80
2	5.17	5.50
3	5.27	5.60
4	3.90	4.80
5	4.85	5.70
6	5.65	5.80
7	8.37	8.40
8	0.00	0.00

Slope = 0.975

Room temperature = 25°C

Sample (1) - (6) Ground waters from various Arabian location

Sample (7) is distilled water saturated with oxygen

Sample (8) is distilled water free of oxygen

TABLE (2)

CHEMICAL ANALYSIS OF WATER SAMPLES

ALL VALUES ARE IN PARTS PER MILLION (PPM) EXCEPT WHERE NOTED

	Sample No. 1	Sample No. 2	Sample No. 3	Sample No. 4	Sample No. 5	Sample No. 6	Sample No. 7	Sample No. 8	Average of 1-6	Correlation Coefficient
T. D. S.	2419	2127	2164	2820	1947	2740	0.0	0.0	2369	0.80
pH Value (dimensionless)	6.87	7.16	7.03	6.82	7.06	7.14	7.0	7.3	7.05	-0.69
Cl^-	848	727	848	970	485	1091	0.0	0.0	828	0.70
$CO_3^=$	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
$HCO_3^=$	134	142	144	237	173	159	0.0	0.0	165	.88
$SO_4^=$	514	501	444	501	436	403	0.0	traces	467	0.70
Na^+	366	400	266	665	400	600	0.0	0.0	450	0.75
Ca^{++}	230	182	172	230	140	230	0.0	0.0	197	0.76
Mg^{++}	100	82	70	82	82	94	0.0	0.0	85	0.75
K^+	40	20	30	20	30	20	0.0	0.0	27	0.72
Dissolved O_2	4.8	5.5	5.6	4.8	5.7	5.8	8.4	0.0	5.6	-0.21
Conductivity micromholcm	41	47	43	50	74	30	10	10	38	0.66
Corrosion rate (mpy)	7.7	6.5	7.1	8.1	7.6	7.4	4.7	1.6	6.3	

TABLE (3)

RANK VALUES FOR CALCULATING SPEARMAN COEFFICIENT (r)

Sample No.	1	2	3	4	5	6	7	8	r
Ranked T.D.S.	3	5	4	1	6	2	7.5	7.5	0.80
pH	7	2	5	8	4	3	6	1	-0.69
Cl^-	3.5	5	3.5	2	6	1	7.5	7.5	0.70
$CO_3^=$	0	0	0	0	0	0	0	0	0.00
$HCO_3^=$	6	5	4	1	2	3	7.5	7.5	0.88
$SO_4^=$	1	2.5	4	2.5	5	6	7.5	7.5	0.70
Na^+	5	3.5	6	1	3.5	2	7.5	7.5	0.75
Ca^{++}	1.5	4	5	1.5	6	1.5	7.5	7.5	0.76
Mg^{++}	1	2.5	6	2.5	2.5	2	7.5	7.5	0.75
K^+	1	4.5	2.5	4.5	2.5	4.5	7.5	7.5	0.72
O_2	5.5	5	4	5.5	3	2	1	8	-0.21
Conductivity	5	3	4	2	1	6	7.5	7.5	0.66
Corrosion Rate	2	6	5	1	3	4	7	8	

TABLE (4)

COUPON DATA FOR CALCULATION OF CORROSION RATE

Coupon No.	Length (dm)	Width (dm)	Diam-eter (dm)	Net Area of Coupon (Sq. dm)	Original Weight (grams)	Final Weight (grams)	Difference in weight (grams)	Corros-ion Rate (mdd)	Corrosion Rate (mpy)
1	0.516	0.381	0.135	0.364	27.052	26.365	0.687	42	7.7
2	0.554	0.381	0.129	0.396	27.623	26.988	0.635	36	6.5
3	0.521	0.381	0.135	0.368	26.553	25.914	0.639	39	7.1
4	0.523	0.381	0.135	0.370	27.174	26.438	0.736	44	8.1
5	0.511	0.381	0.127	0.364	27.138	26.463	0.675	41	7.6
6	0.536	0.381	0.129	0.382	26.808	26.115	0.693	40	7.4
7	0.498	0.381	0.132	0.352	28.713	28.301	0.412	26	4.7
8	0.546	0.381	0.129	0.390	29.283	29.127	0.156	9	1.6

The time of exposure was 44.9 days

Density of iron (Fe) was taken as 7.87 grams/cc (19)

TABLE (5)

MEASUREMENT OF POTENTIAL DIFFERENCES DURING TEST

Cell No.	Reading # (1) (milli volts)	Reading # (2) (milli volts)	Reading # (3) (milli volts)
1	465	100	75
2	490	150	75
3	475	175	55
4	475	200	50
5	390	125	60
6	500	140	40
7	295	660	600
8	150	160	520

(1) Reading # 1 measured at the beginning of the test (March 25, 1975)

(2) Reading # 2 measured at the beginning of the test (April 15, 1975)

(3) Reading # 3 measured at the beginning of the test (May 11, 1975)

TABLE (6)

WATER SAMPLE pH VALUES AT THE BEGINNING AND AT THE END OF THE TEST

Sample No.	pH Value (Beginning of test)	pH Value (End of test)	Corrosion Rate(mdd)	Corrosion Rate (mpy)
1	6.9	5.5	42	7.7
2	7.2	5.0	36	6.5
3	7.0	4.9	39	7.1
4	6.8	4.9	44	8.1
5	7.1	4.9	41	7.6
6	7.1	5.0	40	7.4
7	7.0	7.0	26	4.7
8	7.3	7.3	9	1.6

TABLE (7)

SAMPLE LOCATIONS VS CORROSION RATE

CORROSION RATES AT SAMPLE SITES

No. of Sample & No. of Coupon	Area of Sampling and Type of Sampling	Corrosion Rate (mdd)	Rate of Corrosion (mpy)
1	Al-Jubail - Ice Comp. Well	42	7.7
2	Qatif-Qashuria Well	36	6.5
3	Qatif-A'm Ammar Well	39	7.1
4	University of Pet. & Min. Well	44	8.1
5	Hufof-Cement Comp. Well	41	7.6
6	Dammam - SAFCO Well	40	7.4
7	Distilled Water Saturated with O_2 at 0°C.	26	4.7
8	Distilled Water free of O_2	9	1.6

TABLE (8)

LANGELIER SATURATION INDEX AND CORROSION RATE FOR WATER SAMPLES

Sample No.	Saturation Index	Corrosion Rate (mdd)	Corrosion Rate (mpy)
1	-0.77	42	7.7
2	-0.47	36	6.5
3	-0.74	39	7.1
4	-0.82	44	8.1
5	-0.76	41	7.6
6	-0.42	40	7.4
7	0.00	26	4.7
8	0.00	9	1.6

Rank Correlation Coefficient = 0.92

APPENDIX B

Sample Calculation

APPENDIX B-1

Determination of Dissolved Oxygen :

Winkler technique (6) were used. The experimental procedure was as follows :

1. An aliquot of 300 ml (measured by measuring flask) was used for the test.

2. To the above sample, 2 ml of (4.3 N) $MnSO_4$ and 2 ml of (3.3 N) alkaline iodide reagent were added.

3. By a measuring flask and a pipette, 203 ml of the resulting solution from step (2) were taken to an erlenmeyer flask. Two ml of concentrated H_2SO_4 were added to it. This is to liberate an iodine in an amount equivalent to the oxygen originally dissolved in the sample.

4. The solution prepared at step (3) was titrated with (0.025 N) sodium thiosulfate ($Na_2S_2O_3$).

5. Results of sample-water No. 1 were used to demonstrate the final calculation.
   Volume of $Na_2S_2O_3$ required to neutralize 203 ml of solution prepared at step (3) is equal to 5.19 ml.

Volume corrected for addition of reagents = $(5.19)(\frac{203}{200}) = 5.27$ ml

1 ml $Na_2S_2O_3$ (0.025 N) $\equiv$ 0.2 mg O_2

then 5.27 ml $Na_2S_2O_3$ (0.025 N) $\equiv \frac{(0.2)\times(5.27) \text{ mg } O_2}{200 \text{ ml}}$

1 liter contains $(5)\times(0.2)\times(5.27)$ mg O_2

then concentration of O_2 = 5.27 mg/lt

or 5.27 p.p.m.

APPENDIX B-2

Sample Calcualtion : Effective Area of Coupon

Steel Coupon No. 1

The edges of the coupons were pointed to simplify the calculation of the effective area. In this case the total available area will be reduced by about 4 percent.

Open area of coupon = $(2)\times(L)\times(w)$

= $(2)\times(0.516)\times(0.381)$

= 0.393 sq. dm.

Open area of holes = $2(\frac{\pi}{4})\times(D)^2$

= $(1.57)\times(D)^2$

= $(1.57)\times(0.135)^2$

= 0.029 sq. dm.

Open Net Area = 0.393 - 0.029

= 0.364 sq. dm.

APPENDIX B-3

Sample Calculation : Weight Loss of Coupon

Steel Coupon No. 1

Weight Loss (in grams) = [Original weight before immersion in the sample of water] - [Final weight after cleaning the coupons]

From Table No. 1

Original Weight	=	27.052	grams
Final Weight	=	26.365	grams
Weight Loss	=	0.687	grams
W	=	687	milligrams

APPENDIX B-4

Sample Calculation : Rate of Corrosion

Steel Coupon No. 1

$$\text{Rate of Corrosion (R)} = \frac{W}{(A)\times(t)}$$

Where

W = Weight loss in milligrams

A = Net area of coupon in sq. decimeter

t = Time of exposure in days

R = Rate of corrosion in milligram per sq.decimeter per day (mdd)

To convert mdd to mpy (mils per year) the factor 1.44/density of steel was multiplied by mdd. This factor is taken from Uhlig (19)

From table (1) : density of steel = 7.87 gr/cc

$$\frac{1.44}{7.87} = 0.138$$

$$\text{Rate of Corrosion (R) in mpy} = 0.183 \ \frac{W}{(A)\times(t)}$$

W = 0.687 gram = 687 mg

A = 0.364 sq.dm

t = 44.9 days

$$R = \frac{687}{0.364 \times 44.9} = 42 \text{ mdd}$$

or R= (42) (0.183) = 7.7 mpy

APPENDIX B-5

Sample Calculation:Saturation Index

Take Sample No. 1 as an example :

From Table (2)

T.D.S. = 2419 ppm

Ca^{++} = 230 ppm

$HCO_3^{=}$ = 134 ppm

and From Fig (7) Uhlig (19)

C = 2.34

pCa^{++} = 2.70

pAIK = $\frac{2.60}{7.64}$ = pH calculated

Saturation Index = $pH_{measure} - pH_{cal}$

From table 2, Appendix A, $pH_{measure} = 6.87$

Saturation Index = 6.87 - 7.64 = -0.77

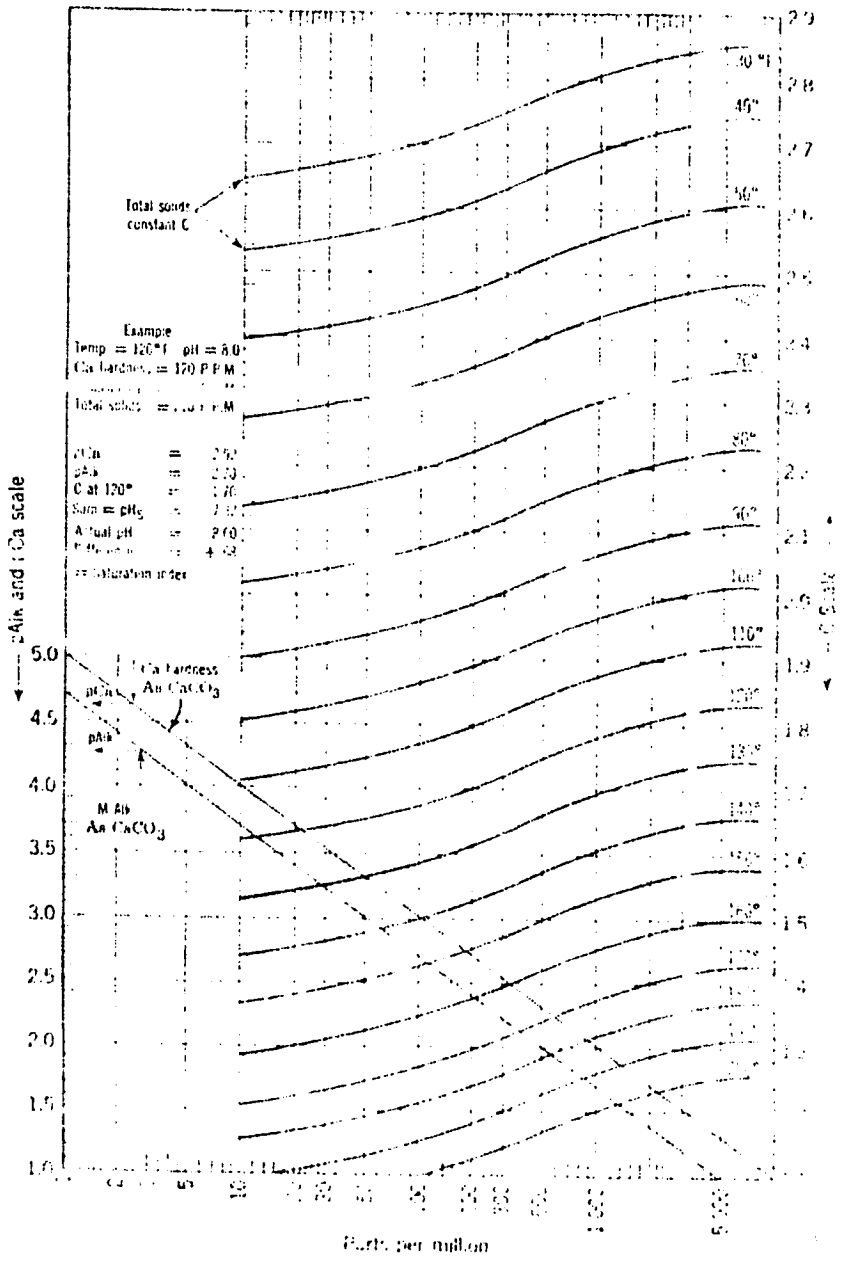

Fig. 7 Chart for Saturation Index

APPENDIX B-6

Calculation of Correlation Coefficient for Saturation Index vs Corrosion Rate

The Correlation Coefficient calculated by using Spearman's formula Kenney and Keeping (8).

$$r = 1 - \frac{6\sum d^2}{N(N^2-1)}$$

Table (9) : Correlation Coefficient (r)

Sample No.	Saturation Index	Corrosion Rate	Rank of Saturation Index (X)	Rank of Corrosion Rate (Y)	Difference (d)	$[d]^2$
1	-0.77	7.7	2	2	0	0
2	-0.47	6.5	5	6	1	1
3	-0.74	7.0	4	5	1	1
4	-0.82	8.1	1	1	0	0
5	-0.76	7.6	3	3	0	0
6	-0.42	7.4	6	4	2	4
7	-0.00	4.8	7.5	7	0.5	0.25
8	0.00	1.63	7.5	8	0.5	0.25

From the formula we have :

r = Correlation Coefficient

d = Difference between two ranks

N = Number of tests of sample

From table (10) we have

$\sum d^2$ = 6.5

N = 8 samples

$$r = 1 - \frac{6\sum d^2}{8(8^2-1)}$$

$$r = 1 - \frac{6\sum d^2}{8[63]}$$

$$= 1 - [0.011905\sum d^2]$$

$$= 1 - [0.011905 \times 6.5] = 1 - 0.0774$$

$$r = 0.9226$$

Values of r are shown in table (2)